

## **Bioaccumulation of Chemical Contaminants in Fishes of Escambia Bay**

Submitted by

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## Introduction

The Bioaccumulation Study is assessing the magnitude of contamination in tissues of marine organisms in the Pensacola Bay region and evaluating the potential human health effects from consumption of locally harvested fish and shellfish. This part of the investigation has focused on the fin fishes in Escambia Bay. A PCB spill in Escambia River and Escambia Bay was documented in 1969 (Duke et al., 1970) and high PCB concentrations have been sporadically reported for the area over the years (e.g., Lewis et al., 2002). Mullet data that were reported in the last EPA progress report for locations above and below the 1969 PCB spill were sent to the Florida Department of Health, along with the previously transferred crab, oyster, mullet data and bass data, for their consideration in issuing a consumption advisory for the lower Escambia River and upper Escambia Bay. This resulted in the issuance of a fish consumption advisory for PCBs in largemouth bass and mullet for the lower Escambia River. In this report, data on additional samples from Escambia Bay are presented, suggesting the problem may not be restricted to the river only, and that species other than mullet and bass are affected.

One other study conducted in Florida waters that has taken a comprehensive examination of accumulation of PCBs and PBDEs in estuarine fishes of Indian River Lagoon was recently published (Johnson-Retrepo et al., 2005). PCB and PBDE concentrations were documented to have increased with trophic status of the fishes, inferred from known life histories and feeding ecology, and to have increased over time. Three of the species studied, Striped Mullet (*Mugil cephalus*), Speckled Trout (*Cynoscion nebulosus*), and Redfish (Red Drum; *Sciaenops ocellatus*) were also sampled for this investigation of Pensacola and Perdido Bays, and the average data for Pensacola Bay shows substantially higher concentrations of contamination. However, the averages mask the elevated spatial concentrations of these pollutants in Escambia bay/river and the urban bayous Texar, Chico, and Grande.

Mercury concentrations in aquatic food organisms is also of increasing concern (NSTC, 2004). In the State of Florida, fish consumption advisories currently exist for mercury in all of the regional fresh and coastal waters (<http://www.dep.state.fl.us/labs/mercury/index.htm>) with consumption bans in some areas and for larger individuals of some species (e.g., King Mackerel). Mercury concentrations in Speckled Trout were recently assessed for Pensacola and Choctawhatchee Bays (Rider and Adams, 2000). Contaminant concentrations in Pensacola Bay seafood have been reported in earlier parts of this study, some of which have been published in the scientific literature (Karouna-Renier et al., 2007).

## Materials and Methods

During construction of the new Interstate 10 bridge across Escambia Bay, an underwater explosion was used to demolish part of the old bridge structure on either side of the shipping channel, mid bay (30.5172 N, 87.1479 W), resulting in mortality of fishes in the vicinity. These fish were collected by personnel from the Florida Fish and Wildlife Commission and placed on ice for transport to the University of West Florida. Samples were cataloged by size and species. Processing procedures followed methods prescribed in the US EPA document *Guidance for assessing chemical contaminant data for use in fish advisories: fish sampling and analysis* (US EPA, 2000). Individual specimens were processed for all fish large enough to provide sufficient

tissue for analysis. Multiple specimens were sorted into similar-sized composite samples where individuals were too small to provide enough tissue for analysis. All fish were measured and weighed.

All processing equipment was washed in mild soapy water, rinsed in a sequence of hot tap water, ethanol or propanol, and purified water. Foil sheets were used to cover cutting boards and handle fillets. Stainless steel fillet knives were used to collect bone and skin-free samples. Total fillet weight was recorded, tissues were macerated in a Foss Tecator tissue homgenizer, and the weight of homogenized tissue added to certified, clean sample jars (200 or 500 ml) was recorded. Where composites were made, equal portions of each fish were added to the composite homgenate.

Tissue samples were kept frozen until transport on ice to Pace Analytical Laboratories, MN for analysis of Dioxin-Furans (DF), Polychlorinated Biphenyls (PCBs), and trace metals and total Mercury (Hg). Toxic equivalent quotients (TEQ) were calculated for DF (TEQ<sub>DF</sub>), Dioxin-like co-planer PCBs (TEQ<sub>P</sub>), and combined DF and Dioxin-like PCBs (TEQ<sub>DFP</sub>) using values in van den Berg et al. (1998).

## Results

Five species of fish were obtained from the blast site, including 9 individuals of sheepshead (*Archosargus probatocephalus*), 7 individuals of white trout (*Cynoscion arenarius*) as a composite sample of 4 and 3 individuals, 2 individuals of spotted seatrout (*Cynoscion nebulosus*), three composites of 6, 2, and 2 individuals of croaker (*Micropogonias undulatus*), and 4 individuals of mullet (*Mugil cephalus*) (Table 1). TEQ values are indicative of the relative contribution of Dioxin-Furans and PCBs to the total TEQ value for dioxin-Furans and the Dioxin-like PCBs (Table 2). Eight samples exceeded the EPA TEQ screening threshold of 0.26 ng/kg for Dioxin-Furans only, and none of these were above 0.5 ng/kg. The TEQ for the dioxin-like PCBs however ranged from low values for the white and spotted sea trout (0.778-4.22 ng/kg) to the highest value recorded for a mullet at 75.0pg/kg, or nearly 300 times the EPA screening threshold for total TEQ (Table 2; Figure 1).

All of the samples exceeded the EPA screening threshold of 20 ng/g total PCBs, with the lowest values recorded in the spotted sea trout (26 and 27 pg/g), and the highest values recorded in the mullet samples (284-1580 pg/g) (Table 2; Figure 2). With the exception of the spotted sea trout values, all of these fish tissue samples also exceeded the State of Florida threshold of 50 ng/g, with the highest mullet sample more than 30 times that level. Despite shifts in PCB congener proportions due to selective microbial degradation (Johnson et al., 2006) and differential partitioning into biomass, the homolog patterns of the total PCBs in these samples were very similar to Arochlor 1254 (Figures 3 and 4), the compound documented in the spill from 1969 (Duke et al., 1970). Previous comparison of skin-on to skin-off mullet fillets indicated the PCB concentrations were approximately doubled by including the skin. The samples in this investigation were all skin-off fillets.

The concentration of trace metals, including Mercury were all low for these samples. The highest Mercury concentrations found were in the trouts ranging from 0.1-0.19 mg/Kg tissue, below the EPA screening threshold of 0.4 mg/kg tissue. These fish were however, relatively small (Table 1) and so would not have the higher levels previously reported for larger specimens of this species in the Pensacola Bay system (up to 0.64 mg/Kg).

## Acknowledgements

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Table 1. Sample characteristics of fish collected at the I-10 bridge over Escambia Bay, Florida.

DATE	ZONE	SPECIES	COMPOSITE	FISH_NO	LENGTH (mm)	WEIGHT (g)	SEX
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917M	1	245	280	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917I	1	255	340	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917S	1	310	610	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917J	1	312	550	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917K	1	345	700	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917O	1	420	1350	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917L	1	440	1580	
9/14/07	Esc. I-10 Bridge	<i>Archosargus probatocephalus</i>	070917N	1	455	1770	M
9/14/07	Esc. I-10 Bridge	<i>Cynoscion arenarius</i>	070917F	4*	295.5	237.5	F
9/14/07	Esc. I-10 Bridge	<i>Cynoscion arenarius</i>	070917U	1	335	330	F
9/14/07	Esc. I-10 Bridge	<i>Cynoscion arenarius</i>	070917T	1	350	440	F
9/14/07	Esc. I-10 Bridge	<i>Cynoscion arenarius</i>	070917E	1	360	460	F
9/14/07	Esc. I-10 Bridge	<i>Cynoscion nebulosus</i>	070917H	1	354	350	F
9/14/07	Esc. I-10 Bridge	<i>Cynoscion nebulosus</i>	070917G	1	455	820	F
9/14/07	Esc. I-10 Bridge	<i>Micropogonias undulatus</i>	070917R	6*	201.8	99.81	
9/14/07	Esc. I-10 Bridge	<i>Micropogonias undulatus</i>	070917Q	2*	222.5	130	
9/14/07	Esc. I-10 Bridge	<i>Micropogonias undulatus</i>	070917P	2*	265	245	
9/14/07	Esc. I-10 Bridge	<i>Mugil cephalus</i>	070917D	1	408	750	F
9/14/07	Esc. I-10 Bridge	<i>Mugil cephalus</i>	070917C	1	424	750	F
9/14/07	Esc. I-10 Bridge	<i>Mugil cephalus</i>	070917A	1	450	930	F
9/14/07	Esc. I-10 Bridge	<i>Mugil cephalus</i>	070917B	1	470	1010	F

\*Samples are composites of the indicated number of individuals. Length and weights for these samples are averages.

Table 2. Toxic equivalency quotients for dioxins and furans (TEQ<sub>DF</sub>) co-planar dioxin-like PCBs (TEQ<sub>P</sub>), combined dioxin furans and PCBs (TEQ<sub>DFP</sub>), and total PCBs for the samples listed in Table 1.

SPECIES	COMPOSITE	% lipid	TEQ <sub>DF</sub> ng/kg	TEQ <sub>P</sub> ng/kg	TEQ <sub>DFP</sub> ng/kg	Total PCBs ng/g
<i>Archosargus probatocephalus</i>	070917M	1	0.27	2.324	2.594	41.1
<i>Archosargus probatocephalus</i>	070917I	0.8	0.19	3.031	3.221	54.1
<i>Archosargus probatocephalus</i>	070917S	1.8	0.4	4.183	4.583	173.0
<i>Archosargus probatocephalus</i>	070917J	0.7	0.17	5.176	5.346	87.7
<i>Archosargus probatocephalus</i>	070917K	0.7	0.17	4.986	5.156	83.7
<i>Archosargus probatocephalus</i>	070917O	0.6	0.16	3.202	3.362	73.6
<i>Archosargus probatocephalus</i>	070917L	2.6	0.46	12.489	12.949	192.0
<i>Archosargus probatocephalus</i>	070917N	1.6	0.36	6.019	6.379	165.0
<i>Cynoscion arenarius</i>	070917F	0.3	0.19	1.751	1.941	336.0
<i>Cynoscion arenarius</i>	070917U	0.6	0.16	4.218	4.378	192.0
<i>Cynoscion arenarius</i>	070917T	0.3	0.12	1.063	1.183	70.9
<i>Cynoscion arenarius</i>	070917E	0.6	0.19	3.715	3.905	105.0
<i>Cynoscion nebulosus</i>	070917H	0.2	0.16	0.793	0.953	27.0
<i>Cynoscion nebulosus</i>	070917G	0.3	0.2	0.778	0.978	26.3
<i>Micropogonias undulatus</i>	070917R	2.4	0.24	3.768	4.008	303.0
<i>Micropogonias undulatus</i>	070917Q	1.5	0.23	2.947	3.177	174.0
<i>Micropogonias undulatus</i>	070917P	3.4	0.34	5.806	6.146	274.0
<i>Mugil cephalus</i>	070917D	4.4	0.42	22.053	22.473	678.0
<i>Mugil cephalus</i>	070917C	2.2	0.27	43.226	43.496	1010.0
<i>Mugil cephalus</i>	070917A	3.9	0.26	13.202	13.462	284.0
<i>Mugil cephalus</i>	070917B	3.3	0.3	75.005	75.305	1580.0

US EPA screening level for TEQ<sub>DFP</sub> = 0.26 ng/kg.

State of Florida screening level for TEQ<sub>DFP</sub> has not been established.

US EPA screening level for total PCB = 20 ng/g.

State of Florida screening level for total PCB = 50 ng/g.

Table 3. Total PCBs and concentrations of PCB homologs for the samples listed in Table 1.

SPECIES	Sample	Total PCBs ng/kg	Mono ng/kg	Di ng/kg	Tri ng/kg	Tetra ng/kg	Penta ng/kg	Hexa ng/kg	Hepta ng/kg	Octa ng/kg	Nona ng/kg	Deca ng/kg
<i>A. probatocephalus</i>	070917M	41100	8.26	136	482	4840	14800	13200	1580	106	16.7	11.1
<i>A. probatocephalus</i>	070917I	54100	9.91	157	623	7260	19900	18100	2270	163	22.4	13.5
<i>A. probatocephalus</i>	070917S	173000	23.4	248	1240	23300	67200	68400	6770	477	55.9	30.4
<i>A. probatocephalus</i>	070917J	87700	14.9	184	848	12300	32900	31700	3540	267	33	15.7
<i>A. probatocephalus</i>	070917K	83700	11	147	674	11100	32700	30100	3300	234	30.7	18.2
<i>A. probatocephalus</i>	070917O	73600	10.5	196	604	7810	27500	28100	3210	218	29.6	16.5
<i>A. probatocephalus</i>	070917L	192000	19.3	223	1270	25000	76500	73900	8710	649	79.8	41.8
<i>A. probatocephalus</i>	070917N	165000	17.8	219	1060	18900	66900	63000	8630	701	101	66.6
<i>C. arenarius</i>	070917F	336000	7.21	169	691	3260	10500	11100	1580	174	27.2	17.4
<i>C. arenarius</i>	070917U	192000	41	645	3730	25900	66400	78300	9940	959	128	58.9
<i>C. arenarius</i>	070917T	70900	15.2	280	1380	9500	23900	27000	2970	298	18.4	20.3
<i>C. arenarius</i>	070917E	105000	21	353	1930	13200	38800	38700	5480	569	81.1	42.5
<i>C. nebulosus</i>	070917H	27000	7.13	164	669	3620	8510	7330	892	84.3	12.8	10.6
<i>C. nebulosus</i>	070917G	26300	5.81	154	586	3290	7870	7340	1010	123	21.9	17.8
<i>M. undulatus</i>	070917R	303000	102	1350	8390	59100	127000	91500	9030	637	67.7	44
<i>M. undulatus</i>	070917Q	174000	94	1230	7320	34100	65200	54700	5460	438	58.2	43
<i>M. undulatus</i>	070917P	274000	161	1960	10700	51900	103000	90200	9260	748	87	59.5
<i>M. cephalus</i>	070917D	678000	156	2000	13800	128000	273000	223000	29800	2380	274	138
<i>M. cephalus</i>	070917C	1010000	201	2860	22500	198000	437000	298000	40700	3440	400	154
<i>M. cephalus</i>	070917A	284000	132	1460	7990	53700	117000	87000	11100	1120	151	73.8
<i>M. cephalus</i>	070917B	1580000	224	2720	21600	273000	683000	518000	73100	6600	672	350

Table 4. Trace metal concentrations in the fish samples from Table 1.

SPECIES	COMPOSITE	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Hg mg/kg
<i>Archosargus probatocephalus</i>	070917M	0.9200	0.0081	0.1900	0.0240	0.0250
<i>Archosargus probatocephalus</i>	070917I	1.2000	0.0081	0.2100	0.0240	0.0300
<i>Archosargus probatocephalus</i>	070917S	1.2000	0.0081	0.1800	0.0240	0.0350
<i>Archosargus probatocephalus</i>	070917J	1.7000	0.0081	0.3300	0.0240	0.0350
<i>Archosargus probatocephalus</i>	070917K	2.0000	0.0081	0.7900	0.0240	0.0390
<i>Archosargus probatocephalus</i>	070917O	0.6800	0.0110	0.1600	0.0240	0.0850
<i>Archosargus probatocephalus</i>	070917L	1.3000	0.0081	0.2100	0.0240	0.0890
<i>Archosargus probatocephalus</i>	070917N	1.2000	0.0081	0.2400	0.0240	0.0920
<i>Cynoscion arenarius</i>	070917F	0.2100	0.0081	0.3000	0.0240	0.1900
<i>Cynoscion arenarius</i>	070917U	0.2800	0.0081	0.1300	0.0240	0.1400
<i>Cynoscion arenarius</i>	070917T	0.1800	0.0081	0.1400	0.0240	0.1200
<i>Cynoscion arenarius</i>	070917E	0.1500	0.0081	0.1300	0.0240	0.1700
<i>Cynoscion nebulosus</i>	070917H	0.3000	0.0081	0.2200	0.0240	0.1000
<i>Cynoscion nebulosus</i>	070917G	0.1900	0.0081	0.1400	0.0250	0.1700
<i>Micropogonias undulatus</i>	070917R	1.0000	0.0081	0.1600	0.0240	0.0170
<i>Micropogonias undulatus</i>	070917Q	1.5000	0.0081	0.4400	0.0240	0.0230
<i>Micropogonias undulatus</i>	070917P	1.1000	0.0081	0.1900	0.0240	0.0390
<i>Mugil cephalus</i>	070917D	0.8700	0.0081	0.2400	0.0240	0.0095
<i>Mugil cephalus</i>	070917C	0.7300	0.0081	0.1700	0.0240	0.0110
<i>Mugil cephalus</i>	070917A	0.5300	0.0100	0.2900	0.0240	0.0130
<i>Mugil cephalus</i>	070917B	1.3000	0.0081	0.1900	0.0240	0.0099

Results in Red are the lower detection limits; sample was below these concentrations

US EPA screening threshold for Hg = 0.4 mg/kg

State of Florida screening threshold for Hg = 0.5 mg/kg

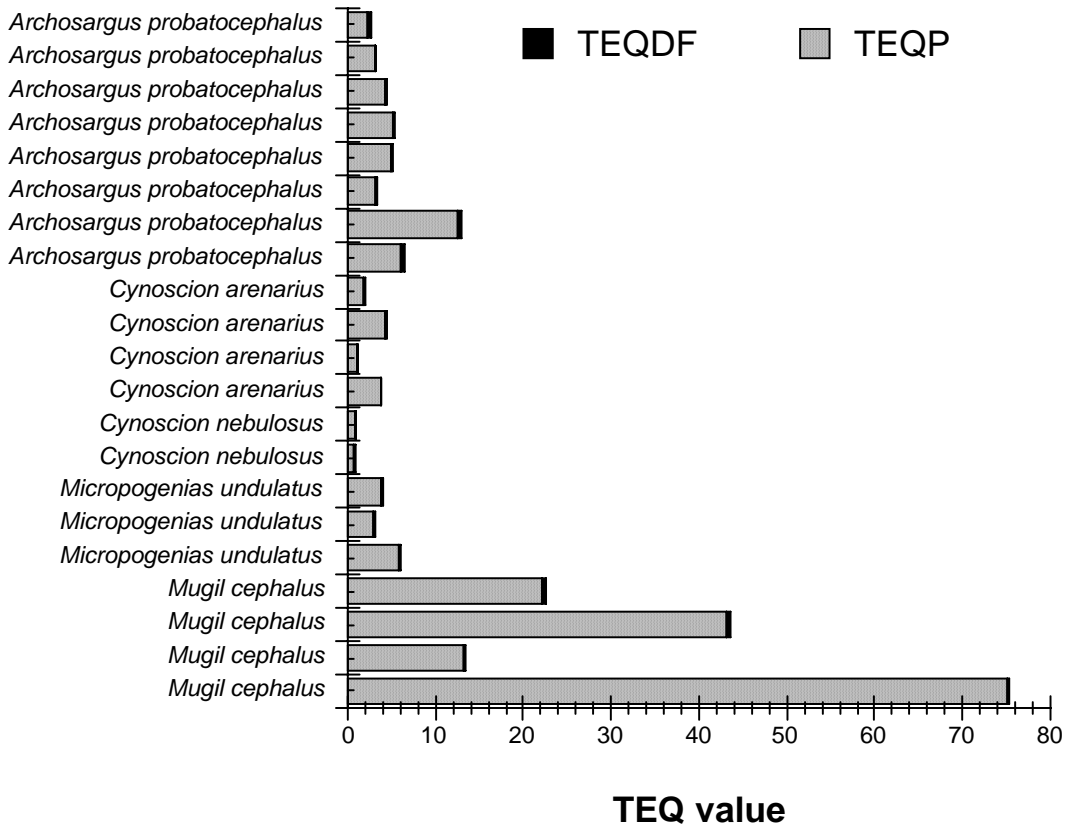


Figure 1. Graphic representation of TEQ values (ng/kg) listed in Table 2.

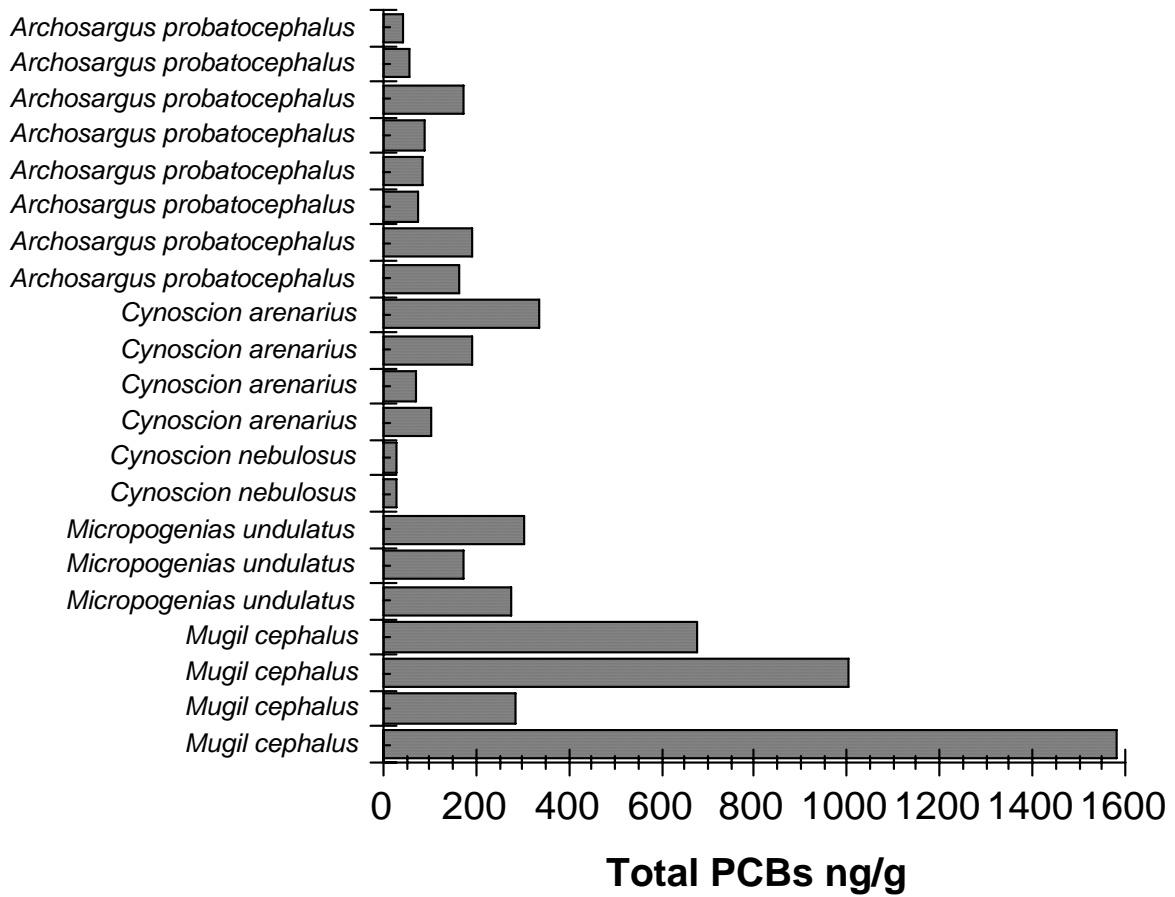


Figure 2. Total PCB concentrations in the fish samples from Table 2.

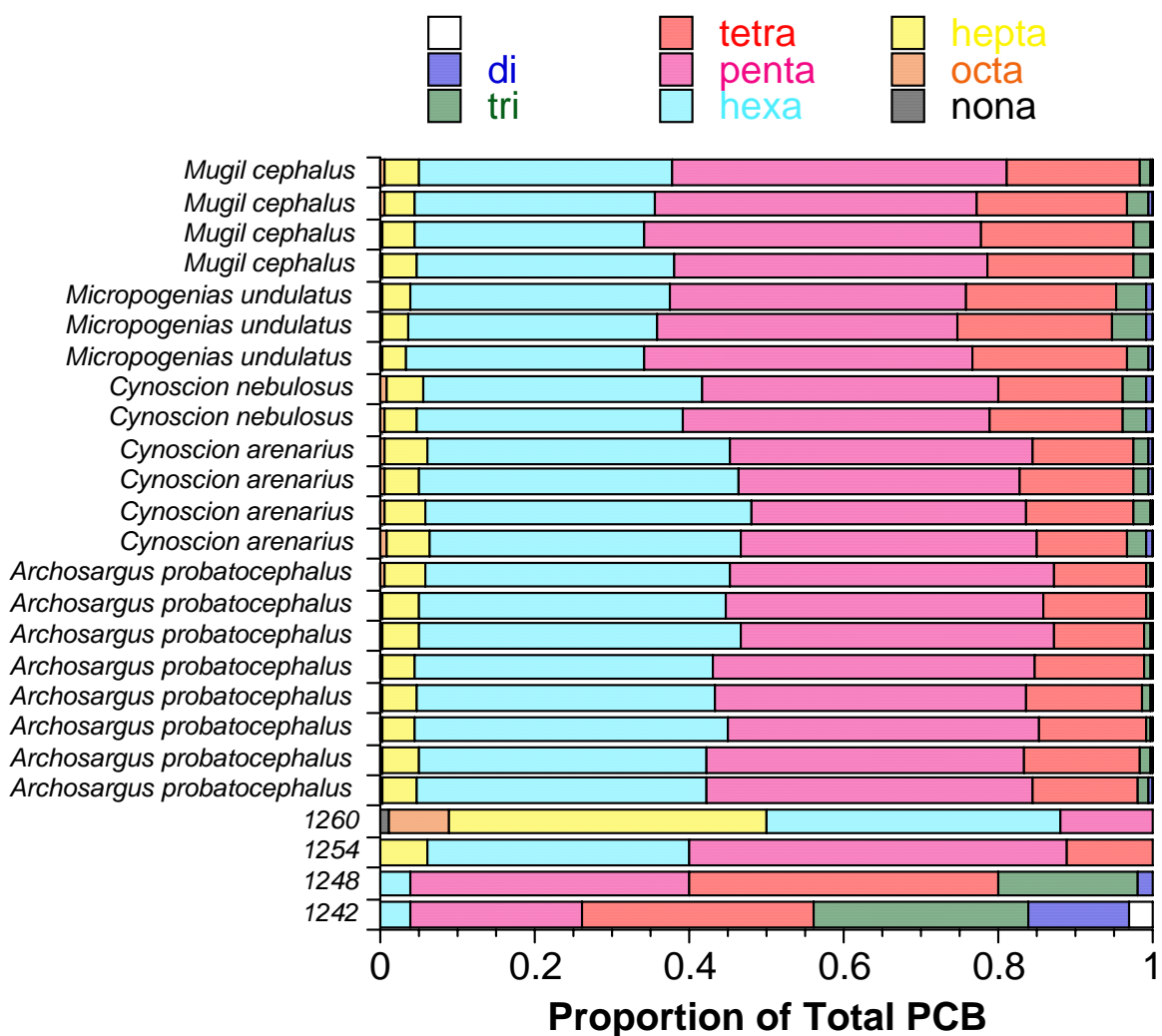


Figure 3. Proportions of homologs (percent of total PCB) in the fish samples. The patterns for the fish tissues most closely match the pattern for Arochlor 1254. Arochlor data from DeGrandchamp & Barron, 2005.

## Hierarchical Clustering

Method = Ward

- Archosargus probatocephalus
- Archosargus probatocephalus
- Archosargus probatocephalus
- Archosargus probatocephalus
- Archosargus probatocephalus
- Archosargus probatocephalus
- Cynoscion arenarius
- Cynoscion arenarius
- 1254
- Micropogonias undulatus
- Mugil cephalus
- Mugil cephalus
- Mugil cephalus
- Mugil cephalus
- Micropogonias undulatus
- Micropogonias undulatus
- Archosargus probatocephalus
- Cynoscion arenarius
- Cynoscion nebulosus
- Cynoscion arenarius
- Cynoscion nebulosus
- 1242
- 1248
- 1260

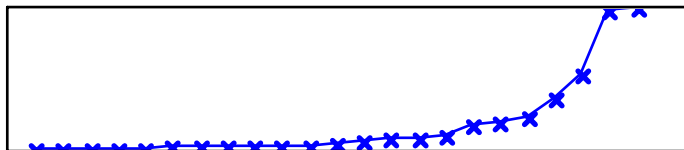
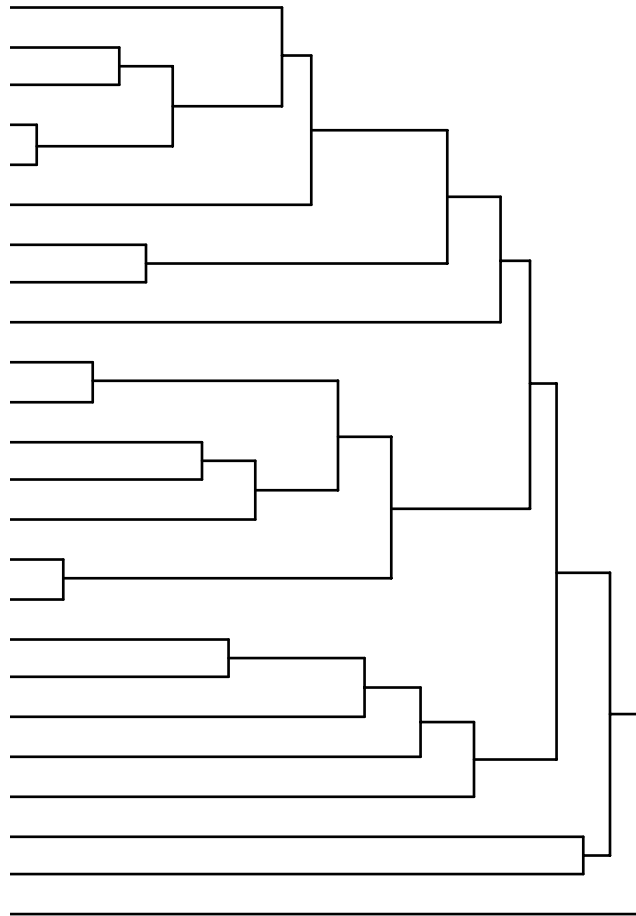


Figure 4. Cluster analysis of the data presented in Figure 3 to match similarities in patterns. Homolog proportions appear to be species specific, indicating different partitioning mechanisms (physiological or trophic) for the different species. Aroclor 1254 clusters in the center of the fish data, while the other Aroclors sit as outgroups at the bottom. Arochlor data from DeGrandechamp & Barron, 2005.